BIOINSPIRED ANTIREFLECTION COATING BY SEEDED SOLUTION-LIQUID-SOLID SYNTHESIS

by

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ABSTRACT

This essay reports on the low-cost seeded solution-liquid-solid (SLS) synthesis anti reflective coating on glass to mimic anti reflective structures in nature. This topic is worth investigation because antireflection coatings have wide range of application from solar cells to glass of daily use, while current strategies of fabrication of anti-reflective coatings are high cost and complicated to operate. Our experimental approach is inspired by the recent developments of SLS growth of silica nanorods on silica particles and solid plains. The main objective of our work is to synthesize ordered silica nanorods array with even size on glass surfaces with anti-reflection properties.

To achieve our objectives, we used spin coating and plasma etching methods to make a layer of highly ordered silica particles in trimethylolpropane ethoxylate triacrylate (ETPTA) as fixed reaction sites. The nanocomposite layer is spin coated from silica particles dispersed in ETPTA on APTCS primed glass slides. The area fraction of silica particles exposed can be tuned by changing the time of etching.

SLS synthesis of ordered silica nanorods array is applied by a one-pot method in water-in-oil emulsion. Tunability of aspect ratio of silica nanorods are investigated by extending reaction time and plasma etching time. We observe the seeded grown silica nanorods array performs an average 4-5% reflectance drops. A brief introduction and explanation of oxygen inhibition phenomena is also introduced in this work.

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1. INTRODUCTION

1.1 Significance & Background

The concept of antireflection was first construed by Lord Rayleigh in the 19th century. Scientists have developed various strategies of achieving anti-reflectivity with the growing demands of manufacturing precise optical instruments and solar cells with high light-capturing efficiency. The wisdom of nature[1-3] has motivated many scientists as the bioinspired antireflection nanotechnologies have attracted intensive research interests. To achieve broadband antireflective coatings (ARC), ideas of highly ordered nanopillars structures in nature like moth eyes are studied, as shown in **Figure 1**. Various strategies have been developed to generate subwavelength nanostructures such as lithography[4], micro replication[5] and chemical vapor deposition[6]. However, these technologies are often complicated to operate and at high costs.

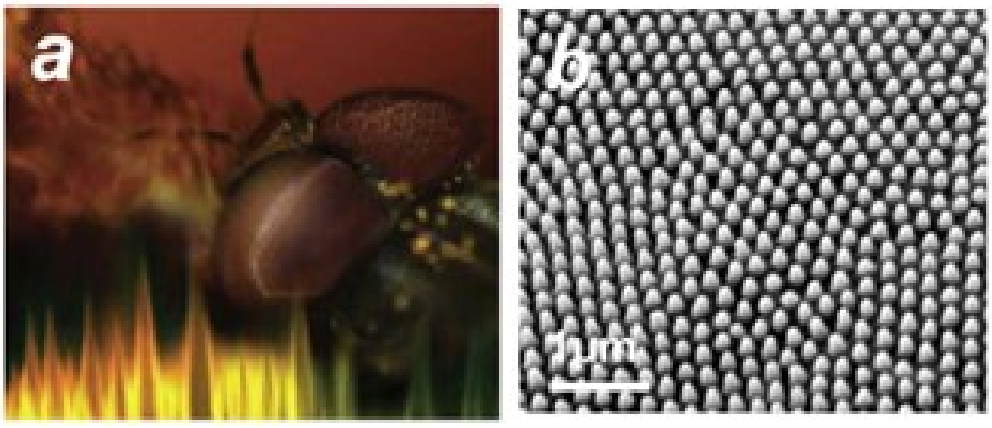

Figure 1 Structure of moth eyes in nature. **(a)** Magnified picture of real moth eyes **(b)** Nanostructure of nanopillars array under SEM. [1] Reprinted with permission from *ACS Nano* **2011**, 5, 9, 6786–6790. *Copyright © 2011 American Chemical Society.*

Solution-liquid-solid (SLS) template growth of non-spherical silica rod-like particles exhibits the great potential of low cost, scalable and straightforward approach of synthesizing ordered subwavelength nanorods array with antireflection properties. Since Imhof *et al.* firstly reported the synthesis of pure silica nanorods in 2011[7], its mechanism and field of application had significantly been studied and broadened. Sharma *et al.* synthesized SLS growth of silica rods on dispersed silica particles[8] and studied the influence of reaction temperature and content of components on reaction rate and shape control of growth of silica nanorods in solution[9]. The growth of silica rods is also extended to other solid particles with different shapes, like titanium dioxide, APTES particles or silica particles[9], and form from hexapods structures[10] to matchstick structures[11], as shown in **Figure 2**. Recently He *et al.* expanded the bases of emulsion attachment from particles to 2D surfaces of ITO, FTO and even pristine glass[12], as shown in **Figure 3.** These findings ensure the feasibility of synthesizing a periodic array of silica nanorods on 2D surfaces to achieve anti-reflectivity.

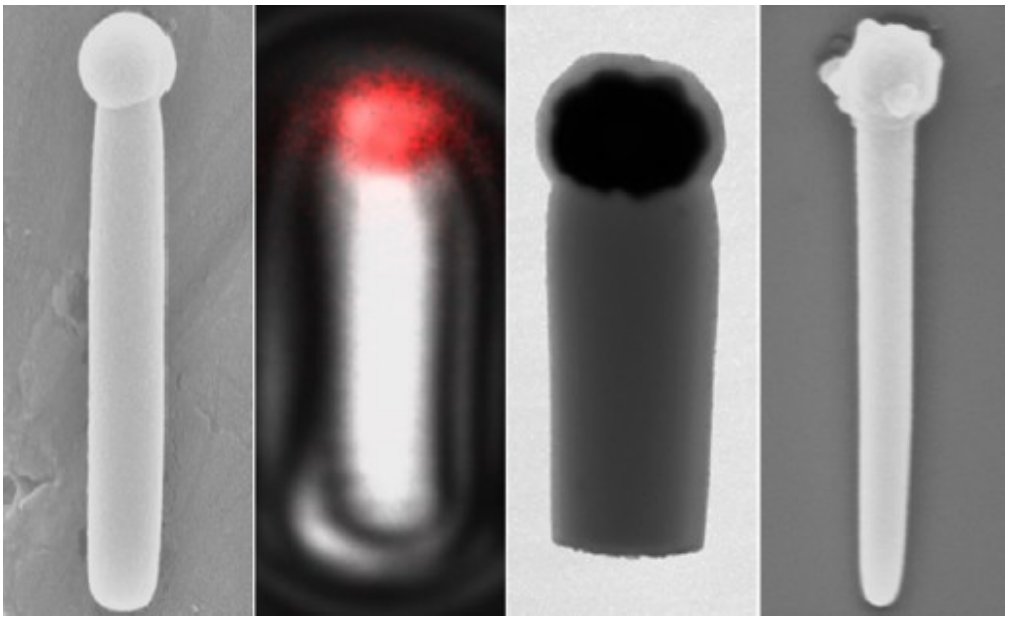

Figure 2 Seeded Growth of Silica Rods from Silica-Coated Particles[11] Reprinted with

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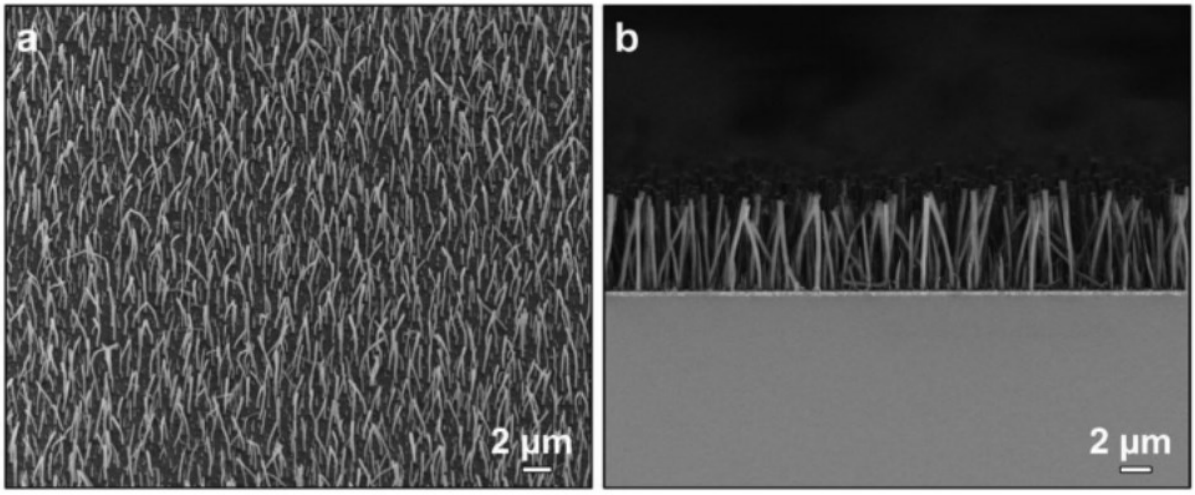

Figure 3 Seeded SLS Growth of Silica Nanorods Array on ITO Glass under SEM, viewed from different directions[12] Reprinted with permission from *Adv. Sci.* **2020**, 7, 2000310. *Copyright © 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.*

1.2 Objectives

In this work, the solid-liquid-solution (SLS) synthesis, spin coating and oxygen plasma etching methods are combined and applied to synthesize silica nanorods arrays periodically with uniform length on glass substrates. Monodispersed silica nanoparticles in 300nm diameter are synthesized by Stober method[13] and dispersed in hydrophobic ETPTA monomer, which is then spin-coated on glass substrates with step increasing speed stages and polymerized to form a layer of ETPTA polymer containing hexagonal distributed silica particles[14]. Oxygen plasma etching is performed to partially burn down ETPTA polymer and expose the surfaces of buried silica particles to serve as fixed hydrophilic reaction sites for the SLS synthesis of silica nanorods[15]. We mix ammonia, sodium citrate, ethanol and DI water to form emulsion droplets

in a solution of PVP-pentanol as the reaction environment. As the emulsion droplets deposit on exposed silica particle surfaces, TEOS is added and condensed into silicon dioxide inside each emulsion droplet, which macroscopically grows into silica nanorods arrays. UV-vis tests show an average drop of 3-4% in reflectance compared with bare glass slides and reveal the potential of scalable seeded growth ARCs.

2. THEORY

2.1 Anti Reflective Nanopillar Arrays

Anti reflective structures in nature, like moth eyes and cicada wings, are composed of an array of nano pillars. The antireflection properties are highly related to the size of individual pillar units, as shown in **Figure 4**. When the size of individual units is much bigger than the wavelength of light, the incident light will be reflected by a single pillar's surface. When the size of pillars is decreased to match the size of light wavelength, the incident light will bounce between the surfaces of adjacent pillars. This process dissipates the light energy and can have some amount of antireflection properties. When further decreasing the size of pillars to subwavelength level, the pillar array can be equalized with a thick layer with gradient increasing refractive index, which allows incident light to be reflected internally and thus achieves the antireflection.

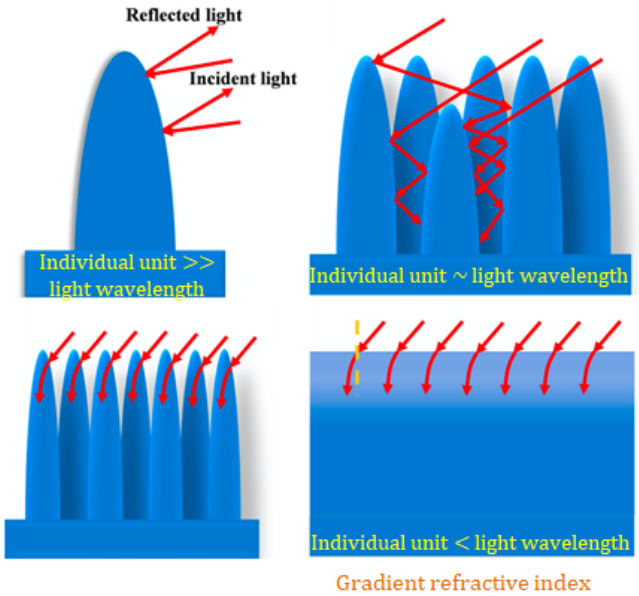

Figure 4 Interaction of Incident Light with Pillars of Different Sizes[16] Reprinted with

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2.2 Oxygen Inhibition of Photo Initiators of Thin Film Monomer

Figure 5 shows a list of reactions during the process of free radical polymerization[17]. The presence of oxygen inhibits polymerization as it reacts with free radicals to form peroxide groups and prevents monomers from crosslinking. Usually, the inhibition of oxygen is negligible during the polymerization of a big volume of monomer since the biggest penetration depth of oxygen inside organic monomer oil is 3μm[18]. But for a thin film of organic monomer oil, this phenomenon is not negligible and polymerization inside a nitrogen bag is crucial.

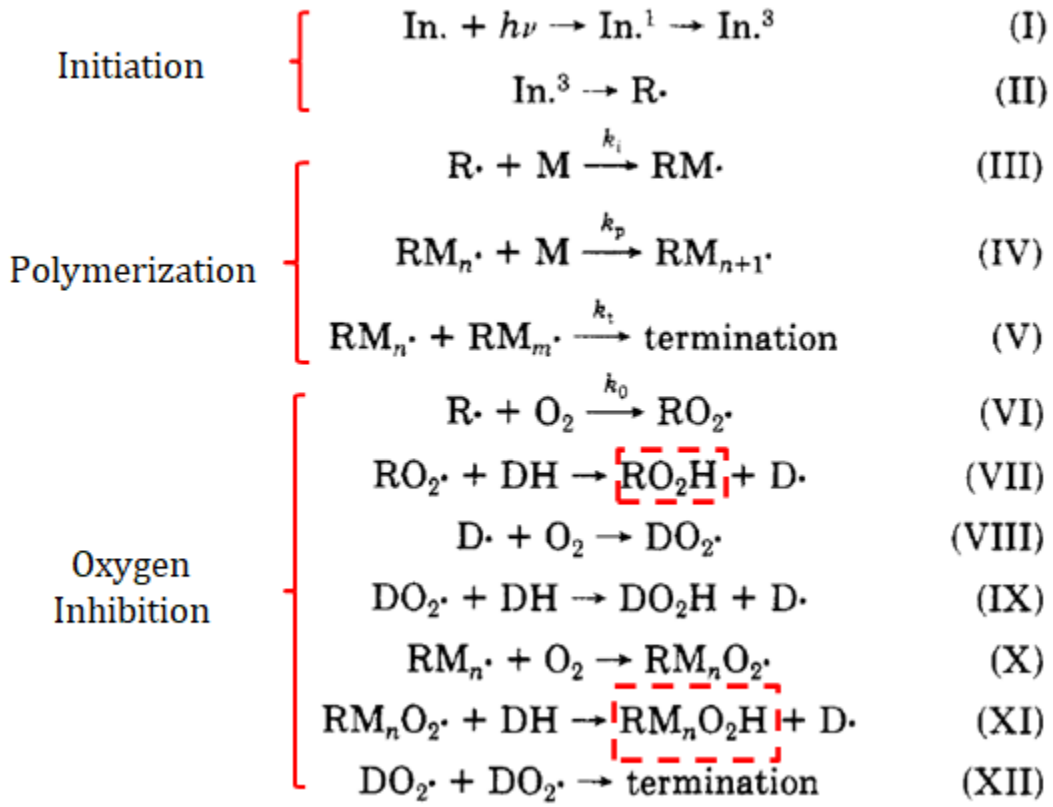

Figure 5 List of Reactions during Free Radical Polymerization and Mechanism of Oxygen Inhibition[17] Reprinted with permission from *Macromolecules* **1985**, 18, 1241-1244.

2.3 Seeded Solution-Liquid-Solid Synthesis of One-directional Silica Nanorods

The solution-liquid-solid growth of silica nanorods, firstly introduced by Imhof *et al.*[7], is typically conducted with the dispersion of silica particles in the water-in-oil emulsion phase, where emulsion droplets are attached to hydrophilic silica particles' surfaces as microreactors. The polyvinylpyrrolidone (PVP, MW=55000) in pentanol serves as a surfactant to stabilize emulsion droplets from condensation. Condensation growth of TEOS occurs on liquid-droplet-solid-silica interface and forms 1D silica nanorods[8], as shown in **Figure 6**.

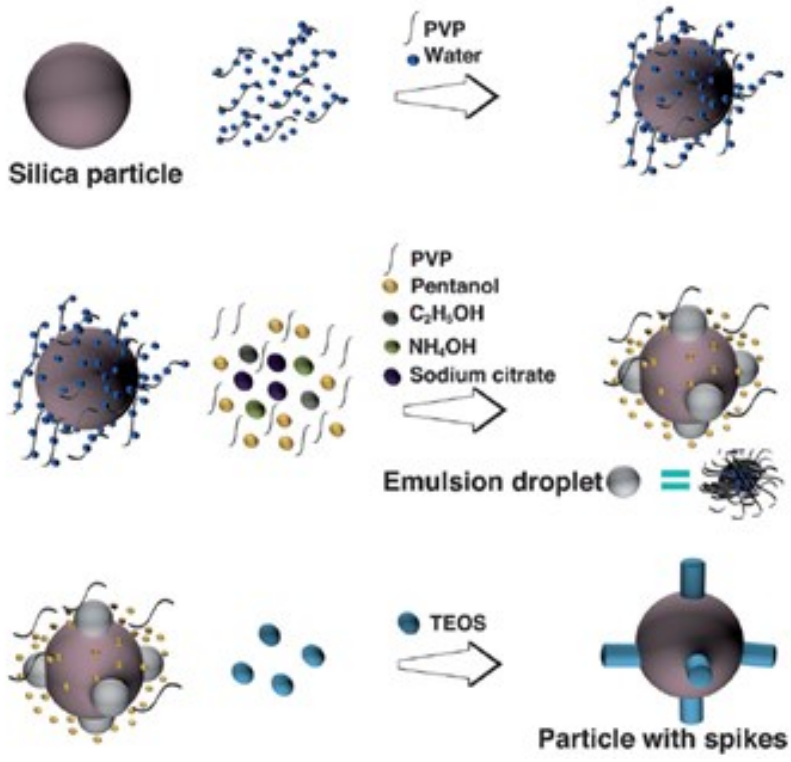

Figure 6 Formation of Water-in-Oil Emulsion, Attachment of Emulsion Droplets on Silica Particles and Condensation of TEOS. Reprinted with permission from *Angew. Chem. Int. Ed.* **2015**, 54, 9011 –9015 *Copyright © 2015 WILEY-VCH Verlag GmbH & Co. KGaA,*

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Inside emulsion droplets, ammonia and sodium citrate together to create a simple environment for condensation of TEOS and control condensation rate with EtOH. TEOS condensate at silica-emulsion interfaces and grow into silica nanorods. The sizes of emulsion droplets change dynamically with the temperature that higher temperature leads to smaller average emulsion droplets size.

The emulsion droplets are attached onto the hydrophilic silica particles' surfaces and the condensation of TEOS takes place at the particle-emulsion interface. The numbers of silica rods grown on each core particle is tunable by changing core particles with different size, shape and kind of materials. The aspect ratio of silica rods is also tunable by changing different reaction time, temperature and amount of components[19].

The growth of silica rods from dispersed particles to 2D hydrophilic surfaces, as shown in **Figure 7.** Similarly, the emulsion droplets are attached onto the surface and grow into an array of nanorods. The average length of nanorods is tunable by extending reaction time[12].

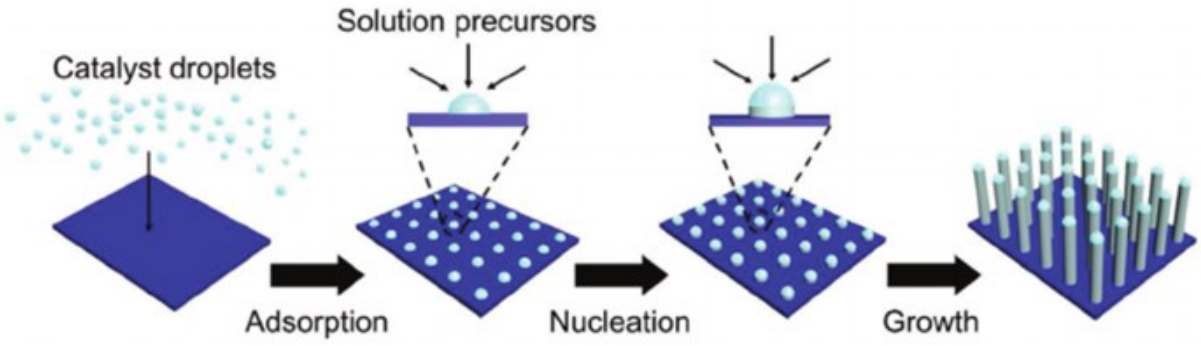

Figure 7 Attachment of Emulsion Droplets on 2D Surface and Growth of Silica Nanorods Array Reprinted with permission from *Adv. Sci.* **2020**, 7, 2000310. *Copyright © 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.*

3. METHODS

3.1 Synthesis of Silica NPs and Preparation of Silica Nanoparticles-ETPTA Solution

The synthesis of the 300nm silica nanoparticles is presented by mixing 16mL ammonia, 12mL deionized water (DIW), 88mL ethanol (EtOH) inside a piranha cleaned bottle. 4.4mL tetra-ethylorthosilicate (TEOS) is added into the bottle, and the solution is stirred at 500rpm overnight. After the reaction, to clean the excess chemicals on the silica particles surface, the 300nm silica nanoparticles are sedimented and redispersed by centrifuge and sonication at 8500rpm in DI water four times, followed by 9000rpm in ethanol for four times. The silica nanoparticles are transferred into a 15ml centrifuge tube.

After redispersion of a certain amount of silica particles, the silica colloid-ethanol solution is mixed with a calculated amount of ETPTA monomer and put in a vacuum oven at 80℃ overnight for complete vaporization of ethanol. When the solution cools down naturally, 2% of Darocur 1173 is added as a photoinitiator. The final volume fraction of silica nanoparticles is controlled to 20%. After filtration with a 5μm syringe filter, the final solution is stored with protection from light.

3.2 Spin Coating, Partial Removal of Polymer and Characterization of ETPTA-Silica NP Layer on Glass Slides

All the substrates of the following steps are glass slides purchased from EMS, cut into 1cm^2 pieces, precleaned by piranha solution and stored in ethanol. Before use, the substrates are blown dried with nitrogen and primed with APTCS by swabbing APTCS with laboratory Q-tips, rinsing with ethanol twice and putting on a hotplate at 90℃ for EtOH to evaporate. The purpose of priming glass substrates with APTCS is to change the surface properties of glass where APTCS serve as molecular linkages to connect with ETPTA polymer during polymerization. Without this step, the ETPTA polymer layer would form wrinkles under oxygen plasma etching.

30μL of the silica-ETPTA solution is dispensed on glass substrates. After tilting and rotating the substrate, to spread the solution to full substrate coverage, the substrate is spin-coated at 200rpm/s for 2min, 300rpm/s for 2min, 1000rpm for 1min, 3000rpm for the 20s and 8000rpm for 6min. Here we apply step increasing speed stages to enhance the evenness of the polymer layer. The spin-coated sample is transferred into a nitrogen bag and exposed under a UV light source for 2min for ETPTA to polymerize.

A homemade plasma, as shown in **Figure 8** etching device performs partial removal of ETPTA polymer with oxygen plasma etching at oxygen's pressure of 40mTorr for 3min. A six-arm diffraction star indicates successful plasma etching under natural light as shown in **Figure 9**. Preliminary observation is performed by Olympus upright microscope to determine

the arrangement and evenness of exposed silica particles. More detailed observation is performed under SEM.

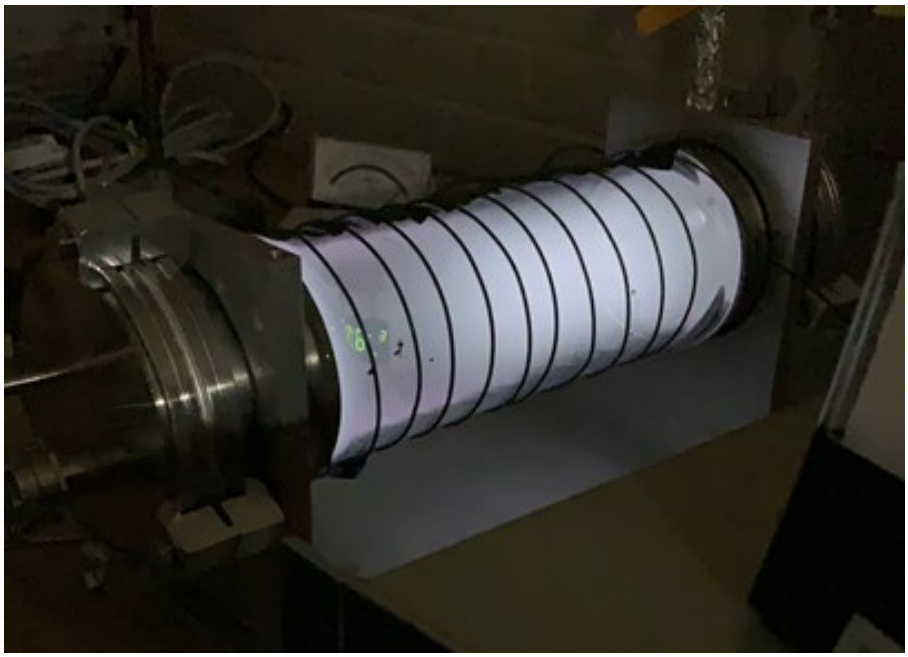

Figure 8 Home Build Plasma Etching Device

3.3 Seeded Growth of Silica Nanorods

Seeded growth of silica nanorods is performed using a one-pot method: 1mL EtOH, 280μL DIW, 100μL sodium citrate solution (1M in DIW) 200μL ammonia is added into 10mL solution of polyvinylpyrrolidone(PVP, MW=55000) in pentanol. The solution is vortexed for 1min and then sonicated for 15mins for a stable emulsion to form.

The glass slide prepared in section 3.3 is added into the emulsion with a piece of plastic taped on the backside to ensure the growth of rods only takes place on the spin-coated side. Then 100μL of tetra-ethylorthosilicate(TEOS) is added into an emulsion under 20s' sonication. The emulsion is put in a vacuum oven at 40℃ or 50℃ for 2h or 4h for silica rods to grow.

After the reaction, the glass slides are put in EtOH and gently shaken for the attached emulsion to fully dissolve. By gradually pouring DIW, the residual sodium citrate salt is also dissolved. Washed samples are dried naturally before property tests.

4. RESULTS AND DISCUSSION

4.1 Ordered Silica Particle Array

The fabrication of non-close-packed colloidal crystals in ETPTA polymer with the hexagonal arrangement is achieved by gradually increasing the spin coating speed. FIGURE shows a piece of a glass slide coated with ETPTA polymer containing 300nm silica particle arrays exhibiting the typical six-arm diffraction with a 60° angle between adjacent arms under white light, which indicates the hexagonal arrangement of silica particles, as shown in **Figure 9.**

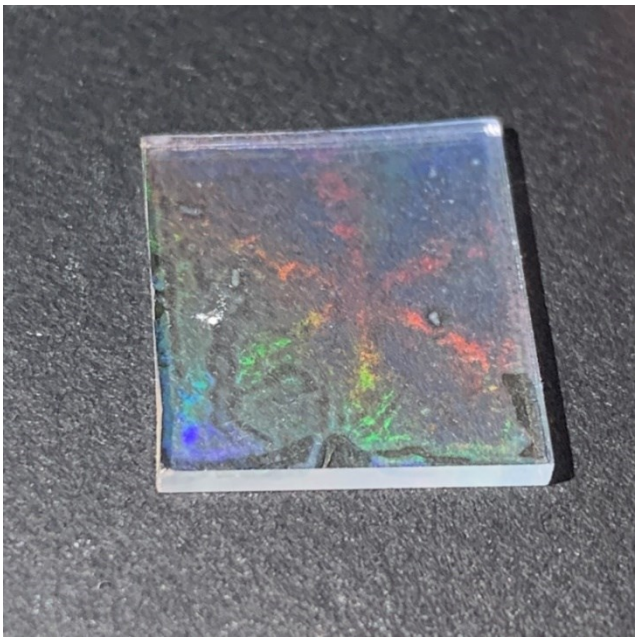

Figure 9 Six-arm Light Diffraction of Spin Coated Silica-ETPTA Nanocomposite Thin Layer under Light

The hexagonal arrangement of silica particles is also evident under the upright microscope, as shown in **Figure 10**. Blocking oxygen during polymerization is crucial for the preparation process. Since the mechanism of ETPTA polymerization is free radical polymerization, oxygen

can significantly inhibit the polymerization because oxygen can absorb free radicals and form peroxide groups at the end of ETPTA monomers. Under normal circumstances like polymerization of a significant drop of ETPTA or polymerization in the water phase, such inhibition is not evident because the penetration of oxygen inside organic oil is several hundred micrometers. However, when polymerizing a thin ETPTA layer with 600nm's thickness, oxygen inhibition is not negligible. A spin-coated ETPTA layer exposed under UV light in the air can be easily washed away by ethanol rinsing.

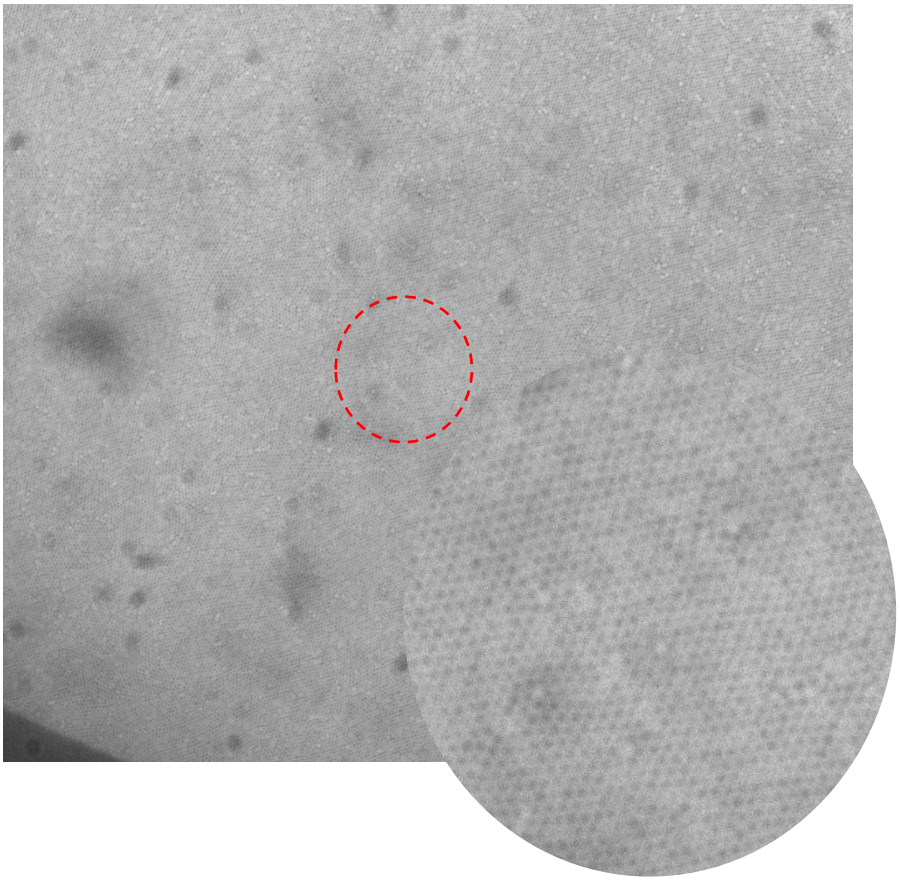

Figure 10 Nanostructures of Spin Coated Silica-ETPTA Nanocomposite Layer under Upright Microscope, 50X Magnification. Insert circle picture shows the further magnified part within red circle.

To expose buried silica particles outside of ETPTA polymer as reaction sites, the spin-coated silica particles crystal in ETPTA is etched by oxygen at 40mTorr, under 25W voltage for 3 minutes using a home built plasma etching device. **Figure 11** shows the morphology of silica particles array after plasma etching under SEM. The black cracks are the boundary of exposed silica particles surfaces and unetched ETPTA polymer, proving the evenness of plasma etching. The area of silica particle exposure can be tuned by reducing or extending etching time, as shown in **Figure 12**.

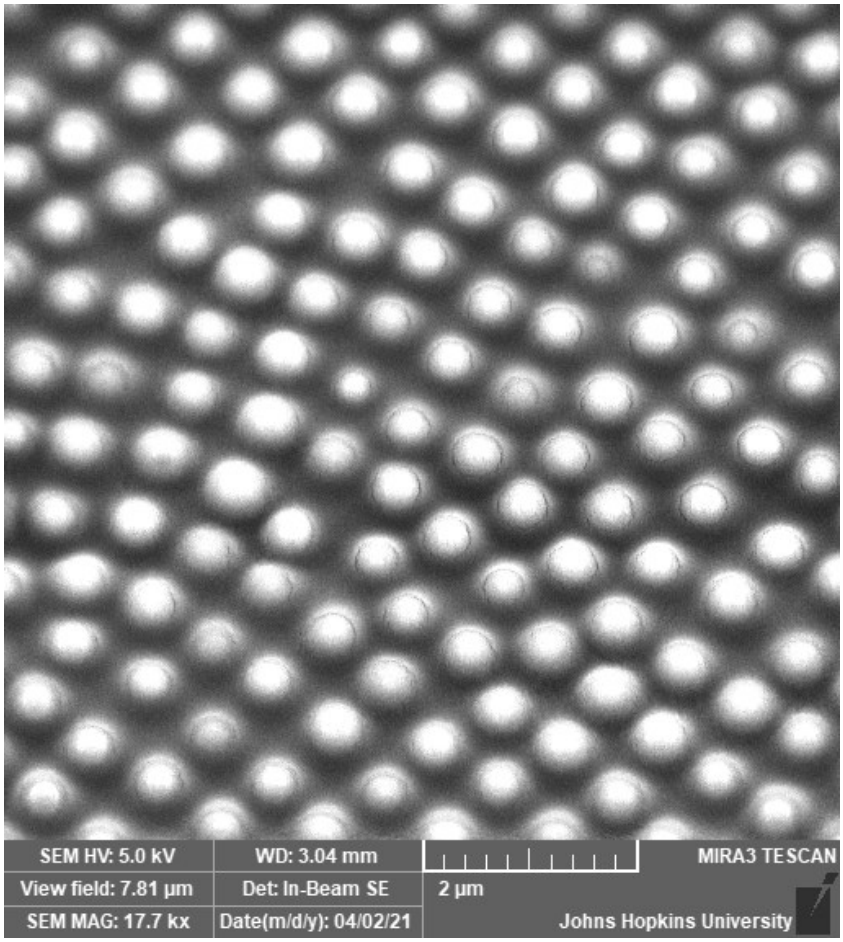

Figure 11 SEM Image of morphology of Silica-ETPTA Nanocomposite Film after Plasma Etching, at 40mTorr, 25W for 3min

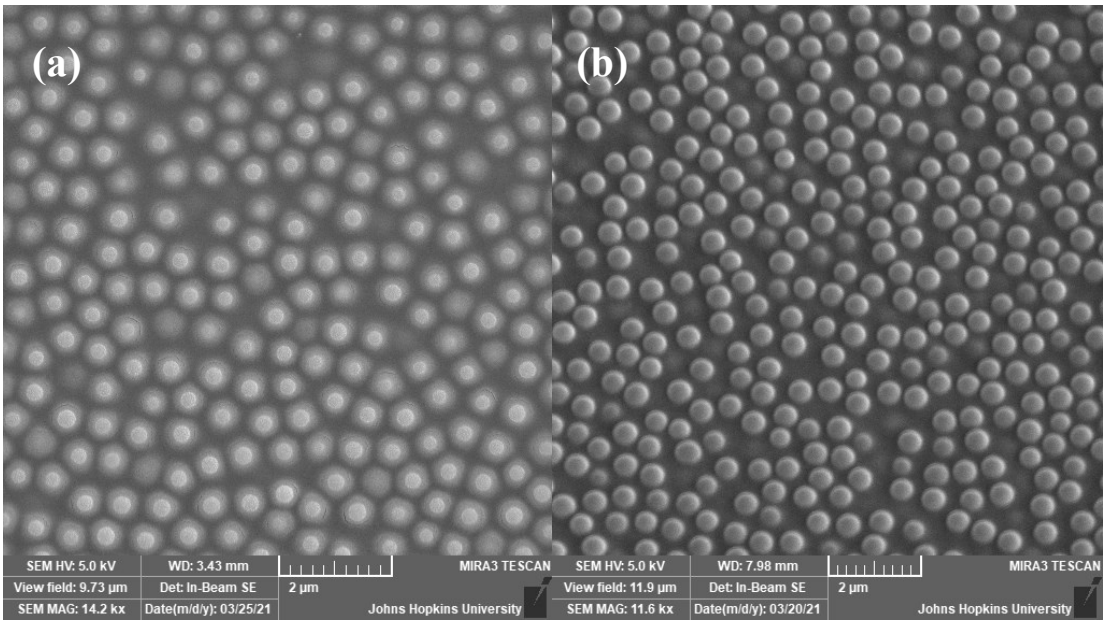

Figure 12 SEM Image of morphology of Silica-ETPTA Nanocomposite Film after Plasma Etching, at 40mTorr, 25W for different etching time **(a)** 2min **(b)** 5min

Priming glass slides with APTCS is also significant for the linkage of ETPTA polymer with the glass surface. Without APTCS, the polymer layer would shrink and form “wrinkles” during the plasma etching process because of heat generated locally, as shown in **Figure 13**.

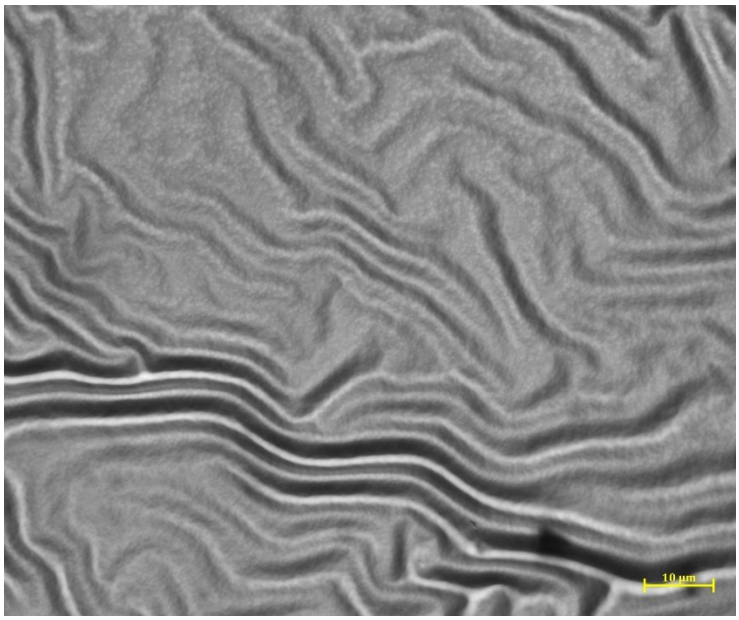

Figure 13 Silica-ETPTA Layer Forms Wrinkles without Priming Glass with APTCS

4.2 Seeded SLS Synthesis of Silica Nanorods

The first reported SLS synthesis of silica nanorods on glass slides, with an ordered hydrophilic reaction sites coating. **Figure 14(a)** shows the SEM image of a typical silica nanorods array grown at 40℃ for 2h. An array of silica nanorods grow vertically on most silica particles with uniform sizes. The tops of silica nanorods slightly bend toward each other because of capillary/Laplace forces during the washing and drying process. Compared with the growth of nanorods under the same condition on new glass's surface without fixed reaction sites, as shown in **Figure 14(b)**, the seeded grown silica nanorods array is more ordered in diameter and more uniform in size, and also have better optical properties as discussed in the following section.

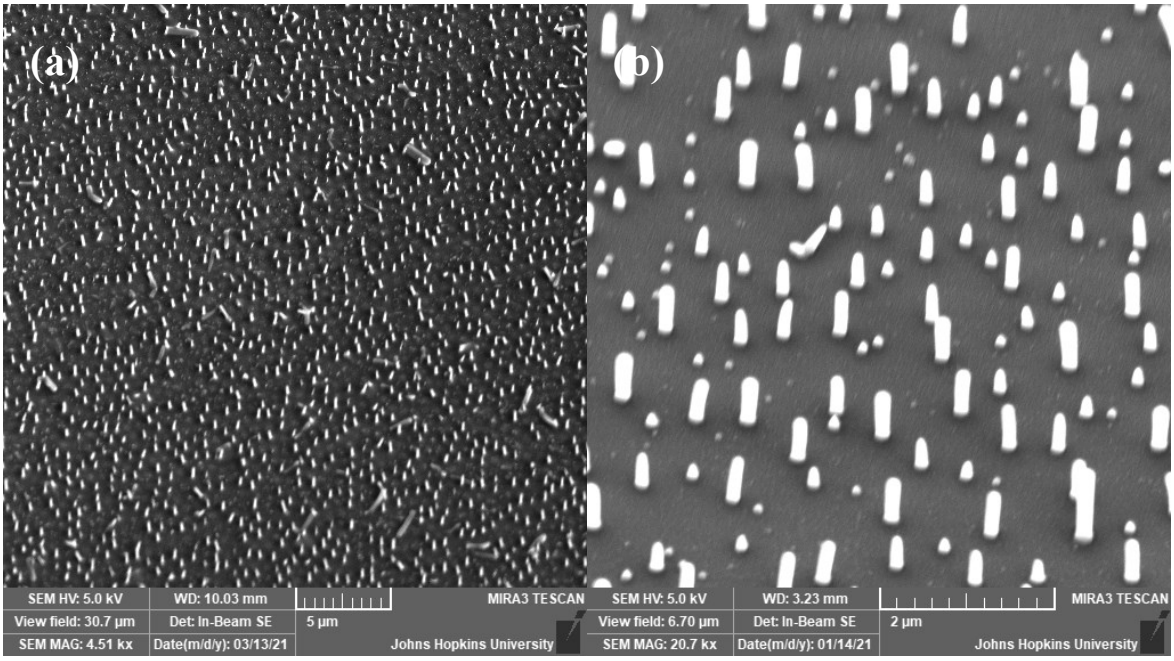

Figure 14 SEM Images of **(a)** Seeded **(b)** Seedless Growth of Silica Nanorods Array at 40℃ for 2h.

According to the mechanism of SLS growth of silica nanorods, the average length of silica nanorods is tunable by extending the reaction time, as shown in the **Figure 15** of nanorods array grown at 40℃ for 4h. The grown rods grow longer and become more bent while their diameter barely changes, consistent with the 1D growth mechanism of SLS growth.

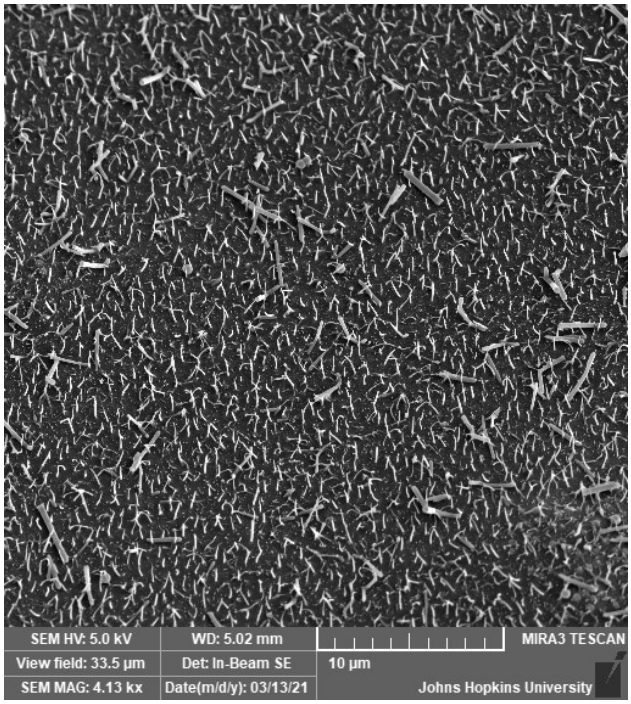

Figure 15 SEM Image of Seeded Growth of Silica Nanorods Array at 40℃ for 4h.

However, the diameter of silica nanorods is not tunable by increasing plasma etching time and exposing more area of silica particles. **Figure 16** shows silica nanorods grown at 40℃ for 2h on a silica particles array with ETPTA polymer etched at 25W for 5min. With more silica particles exposed, the nanorods tend to grow between silica particles indicating the emulsion droplets are no longer attached to each reaction site.

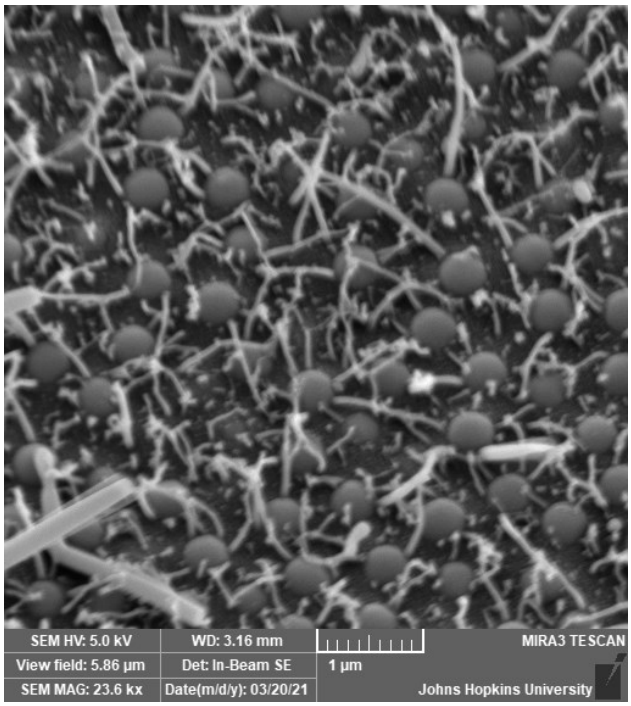

Figure 16 SEM Image of Seeded Growth of Silica Nanorods Array at 40℃ for 2h, with Plasma Etching Time Extended to 5min

4.3 Optical Properties

To analyze the optical properties of silica nanorods arrays grown under different conditions, the transmittance and reflectance of several samples are measured by UV-vis-near-IR spectrometer. **Figure 17** shows the curves of transmittance and reflectance of pristine glass, seeded grown silica nanorods arrays for 2h and 4h, and seedless grown silica nanorods array on pristine glass for 2h in visible light region of 400nm-800nm wavelength.

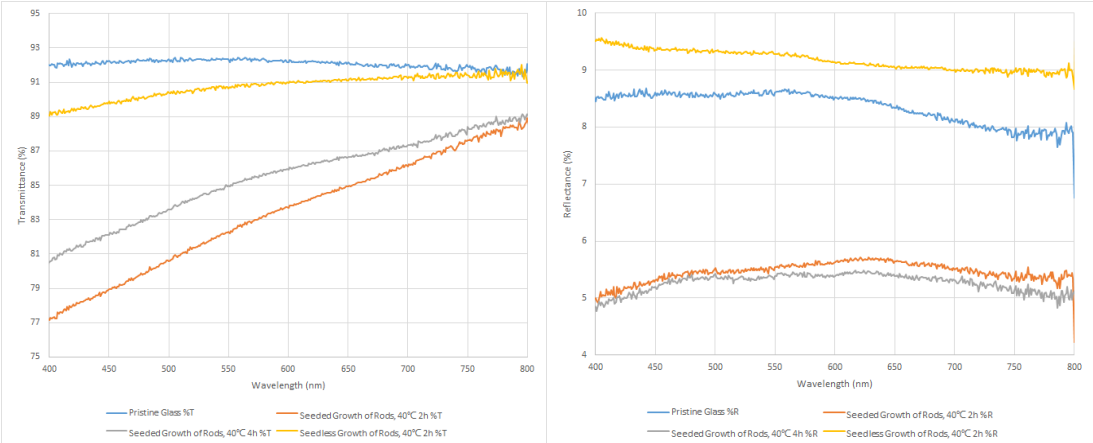

Figure 17 UV-vis Test Results of Transmittance and Reflectance of Pristine Glass (Blue Line), Seeded Grown Nanorods Array at 40°C for 2h (Orange Line), Seeded Grown Nanorods Array at 40°C for 4h (Grey Line), Seedless Grown Nanorods Array on Pristine Glass at 40°C for 2h (Yellow Line).

In this figure, blue lines represent the transmittance and reflectance data of pristine glass as a reference; orange and grey lines are transmittance and reflectance data of silica nanorods arrays grown on seeded reaction sites grown at 40°C for 2h and 4h; yellow lines stands for silica nanorods array grown directly on pristine glass at 40°C for 2h.

Compared with pristine reference glass, the specific group of seeded growth of rods at 40°C for 2h presents good anti-reflection properties with a 4-5% average reflectance drop. The importance of growing silica nanorods on a surface with ordered reaction sites is evident by comparing with yellow and orange lines of seeded and seedless growth of silica nanorods that seedless grown nanorods array does not have anti-reflection properties. Prolonging reaction time to 4h, as indicated by comparing reflectance data of seeded growth of nanorods samples for 2h and 4h, does not significantly change anti-reflection properties. However, the transmittance data indicate room for improvement as all samples with silica nanorod arrays

present loss of transmittance from pristine glass. Turbidity of spin coated silica-ETPTA layers can be reduced in future work by decreasing the thickness of silica-ETPTA nanocomposite film.

5. CONCLUSIONS

This work mainly focuses on the seeded SLS synthesis of silica nanorods array to get antireflection structures. Spin Coating and oxygen plasma etching methods are applied to make a silica-ETPTA polymer layer of ordered silica particles as fixed reaction sites. Solution-liquid-solid are applied to synthesize periodically arranged silica nanorods array. The arrangement and evenness of silica nanorods are improved compared with seedless growth of nanorods on pristine glass. The length of silica nanorods are tunable by increasing reaction time from 2h to 4h but the diameter of nanorods is not tunable by increasing etching time of plasma treatment.

UV-vis tests of nanorods array grown under different conditions show a 4-5% reflectance drop of ordered silica nanorods array from pristine glass, while seedless grown nanorods don't have antireflection properties. Increasing the length of silica nanorods array presents similar antireflection properties. The transmittance drop of silica nanorods array indicates the room of improvement to decrease the turbidity of spin coated silica-ETPTA nanocomposite layer.

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